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Stable multiple emulsions of the W/O/W type, in particular for cosmetic purposes, and process for the production thereof

Description

The invention relates to multiple emulsions of the W/O/W type that can be prepared by phase inversion processes and are suitable for cosmetic and therapeutic purposes. In particular, stable emulsions of the W/O/W type are designed for cosmetic purposes.

Multiple emulsions are an interesting emulsion system for use in cosmetics. They are emulsions that in the inner emulsion phase contain smaller drops of a liquid that either corresponds to the continuous external phase or is similar to it. Two basic types can be differentiated, the oil-in-water-in-oil (O/W/O) emulsions and the water-in-oil-in-water (W/O/W) emulsions. For use in cosmetics, the W/O/W emulsion type is of interest. The O/W/O emulsion type is unsuitable for cosmetic use on account of the high fat content and of the skin sensation and application behavior associated therewith. On account of its construction, the W/O/W type is an intermediate of the conventional O/W and W/O emulsions. The crucial advantage of a W/O/W emulsion compared to other types of emulsion is the combination of the lasting and moisture-donating effect of a W/O emulsion with the pleasant and gentle skin sensation of an O/W emulsion. Since the outer

phase is aqueous, an immediate cooling effect and a moisturizing effect occurs. The internal water phase permits lasting hydration. A further advantage of a W/O/W emulsion compared to a W/O emulsion is the lower viscosity and the easy and rapid spreadability associated therewith. It is not sticky and leaves a pleasant skin sensation. All in all, novel, positive effects in the sensory field are produced on the application of the multiple emulsion.

Multiple emulsions can be produced using the "single-stage" or the "two-stage" processes. The two-stage process has already been described several times (in DE-PS 41 36 699 and by K. Stickdorn et al. in "Parfümerie und Kosmetik" [Perfumery and Cosmetics] 1994, No. 12).

In the context of the present invention, the single-stage phase inversion process in particular is used that is already described in DE 43 43 833 A1. According to this DE-OS, ethoxylated fatty acids, in particular PEG stearate, with up to 200 ethoxylation units are used as emulsifiers for relatively water-rich emulsions with polar vegetable oils as the main component of the oil phase, together with up to 5% of electrolyte in the water phase, and one or more stabilizers. In practice, it is seen that castor oil-containing mixtures principally form stable multiple emulsions, whereas the other mixture examples indicated tend to form O/W emulsions.

The aim of the present invention was therefore to design mixtures and process conditions for the achievement of stable multiple emulsions using a special emulsifier or emulsifier mixture in combination with cosmetically suitable oils, particularly those of natural origin.

The emulsions of the W/O/W type developed for this purpose, which can be prepared by phase inversion processes, are essentially characterized by the following constituents:

(a) at least one nonionic, ethoxylated emulsifier of the PEG-phytosterol type with 5 to 26 ethoxylation units, which has a cloud point between 50 and 110°C and an HLB > 10.

(b) oils with at least 5% by weight (based on the total emulsion) of components that have a polarity < 20 mN/m and an HLB > 10;

(c) stabilizers influencing the viscosity of the emulsion based on mixtures of polar waxes and/or organic hydrogel formers;

and optionally additives useful for the formulation of dermally applicable preparations;

with a phase ratio of at most 35% oil to 65% water.

Further distinctive features of the invention ensue from the following description and the patent claims.

Phase inversion is a method frequently used in practice for emulsion preparation. In general, it is employed for the preparation of O/W emulsions. Such emulsions are distinguished by a particularly small drop size. Moreover, they have a high long-term stability. There are two possibilities for preparing an O/W emulsion with the aid of phase inversion:

- increase in the phase volume until an inversion occurs;
- temperature increase up to the phase inversion temperature (PIT).

If an emulsion is prepared using the PIT, the PIT is the crucial preparation parameter. An O/W emulsion existing at room temperature can invert to the W/O emulsion on temperature increase and after reaching the PIT. On lowering the temperature below the PIT it reinverts again to an O/W emulsion. The higher the PIT, the more stable the O/W emulsion at room temperature. It is ideal if the PIT is between 60-90°C, but at least 20°C above the storage temperature and at most 110°C.

Shinoida discovered that in the case of nonionic ethoxylated emulsifiers the PIT correlates with the "cloud point" (Shinoida, K.; Arai, H. In: Journal of Physical Chemicals 68 (1964), p. 3485). Solutions of nonionic emulsifiers in water become cloudy on exceeding a certain,

sharply defined temperature, which is characteristic of the respective surfactant. The cloud point increases with increasing ethoxylation units. The cloud point can be lowered by addition of salt and increased by addition of alcohol. Emulsifier mixtures enable an adjustment of a certain cloud point and thus also the PIT.

It was possible to determine that for W/O/W emulsions an HLB of normal O/W emulsions (HLB > 10 for emulsifier and oil) is suitable and thus the adjustment of the emulsifier or the balance between hydrophilicity and lipophilicity must be similar.

A stable W/O/W emulsion according to the invention, which is produced using the phase inversion process, is distinguished by the above-mentioned composition, where in particular the interfacial tension of the oil or the oil phase compared to water is used as a basis for the determination of the polarity of the oils or oil components. The interfacial tension indicates the work that must be expended in order to increase the surface area of a liquid by 1 cm. Here, the polarity of an oil is all the higher, the lower the interfacial tension compared to water. Interfacial tensions of the oils compared to water can be determined using a ring measuring device of a digital tensiometer.

Stabilizers used are in particular long-chain, saturated fatty alcohols (C_8–C_{18}) and/or glycerol stearates (glycerol mono/distearates) and/or organic hydrogel formers

(polyacrylates, xanthan gum, alginates etc.).

They influence the viscosity of the emulsion and thus have a crucial influence on the stability.

A phase ratio of at most 35% oil to 65% water offers the possibility of achieving the favorable sensory effects. Quantitative ratios of the emulsifier, consistency-imparting agent, or oil and demineralized water corresponding to 1-8:2-10:5-32:50-92 (in percent by weight) are preferred. In particular, ratios around approximately 3:7: 20:70 can be chosen.

The following additives are expedient for the formulation of a cosmetic formulation:

- use of further oil components, of spreaders and emollients

In order to achieve pleasant application behavior and an optimal skin sensation, further oil components such as vegetable/animal oils and fats, liquid wax esters, fatty acid esters, paraffin oils and/or silicone oils can be employed.

- use of humectants

Glycerol, propylene glycol, butylene glycol, sorbitol etc. are employed in order to prevent water loss.

- use of preservatives and antioxidants

All preservatives and antioxidants suitable for cosmetics can be employed.

- adjustment of the pH

The pH can be adjusted to be skin-friendly to a value, corresponding to the acid protective coat of the skin, of pH 5 to pH 6.5, with suitable substances such as, for example, sodium hydroxide solution, tromethamine or citric acid.

- incorporation of active ingredients

Fat- and water-soluble active ingredients can be incorporated into the fat or water phase.

Active ingredients used are in particular the substances and materials useful for cosmetics. Of course, it is also possible, however, to provide therapeutically useful active ingredients in the form of an emulsion according to the invention.

Starting from the above-mentioned special basic formulation

Ingredients	Indication of weight (%)
emulsifier	3
consistency-imparting agent	7
oil	20
water, demin.	70

the following formulation examples can be mentioned:

Lotion

Ingredients	Weight information (%)
Part A	
PEG-10 soybean sterol	4.0
glycerol monostearate	4.0
cetearyl alcohol	3.0
wheatgerm oil	7.0
avocado oil	7.0
octyl octanoate	2.0
PCL liquid	2.0
preservative	q.s.
Part B	
water, demin.	to 100
butylene glycol	7.0
panthenol 50 P	1.0
allantoin	0.1
Part C	
cyclomethicone	2.0
antioxidants	q.s.
preservative	q.s.
perfume	0.3

Moisturizer

Ingredients	Weight information (%)
Part A	
PEG-16 soybean sterol	4.0
cetearyl alcohol and	
sodium cetearyl sulfate	3.0
beeswax	3.0
castor oil	7.0
wheatgerm oil	7.0
Cetiol V	4.0
phytosqualane	4.0
preservative	q.s.
Part B	
water, demin.	to 100
glycerol	7.0
hydrovitone	1.0
Na D-glucuronate	0.1
carbopol	0.2
hyaluronic acid	0.1
EDETA	0.05
tris	0.2
Part C	
antioxidants	q.s.
preservative	q.s.
perfume	0.3

Preparation of a multiple W/O/W emulsion

For the preparation of a stable multiple emulsion with an optimal yield of multiple drops, according to the phase inversion process optimal phase incorporation in particular is to be observed for the formation of multiple drops: it has been shown that the phase incorporation of water phase and oil/emulsifier phase should expediently take place directly after reaching the PIT of the emulsion or the cloud point of the emulsifier. Subsequently, the emulsion is stirred, whereupon no shear forces must be introduced into the emulsion in order not to interrupt or to disturb the process of phase inversion. Only shortly before the solidification limit of the stabilizers, the mixture is homogenized with minimal shear rate for the attainment of the optimal multiple particle sizes of 10-30 µm. Temperature control during the use of the PIT process is a crucial factor for the formation of multiple drops. It is in each case fixed taking into consideration the determined PIT of the emulsion or the cloud point of the emulsifier. The stirring intensity is determined by two aspects:

- The stirring intensity must be at least so high that all components mix. In principle, air introduction during stirring should be avoided, as this can lead to destabilization. The emulsifier of an emulsion can itself

regulate such air bubbles on the air/liquid interface.

- The stirring intensity must maximally be so high that the phase inversion is not disturbed. No shear forces must be introduced. The introduction of shear forces is avoided by the use, for example, of an inclined blade stirrer.

Homogenization should take place shortly before the solidification points of the consistency-imparting agents. The homogenizer time depends on the desired particle size of 10-30 μm and must be applied to the respective homogenizer system.

Preparation example

The following equipment was employed:
stirrer: Janke & Kunkel, RW 20 with inclined blade stirrer
homogenizer: Janke & Kunkel, Ultra Turrax T 25
stirring vessel: 500 ml beaker
batch: 200 g.

The preparation process used was the hot/hot process.

All substances were weighed into a beaker to an accuracy of 10 mg separately according to part A, B and C (see formulations indicated above) using an analytical balance. Part A and part B were heated separately to at least 85°C in a water bath. After reaching the temperature, part A

was added to part B (or conversely) and mixed with the stirrer at a speed of 200 rpm. The mixture was homogenized at 8000-9500 rpm for 12 seconds at an emulsion temperature of 60°C. Subsequently, it was cooled to 40°C at a speed of the stirrer of 200-500 rpm. Finally, part C was added and the emulsion was brought to room temperature under identical stirring conditions.

Patent claims

1. A multiple emulsion of the W/O/W type that can be prepared by phase inversion processes and is suitable for cosmetic and therapeutic purposes, comprising

(a) at least one nonionic, ethoxylated emulsifier of the PEG-phytosterol type with 5 to 26 ethoxylation units, which has a cloud point between 50 and 110°C and an HLB > 10;

(b) oils with at least 5% by weight (based on the total emulsion) of components that have a polarity < 20 mN/m and an HLB > 10;

(c) stabilizers influencing the viscosity of the emulsion based on mixtures of polar waxes and/or organic hydrogel formers;

and optionally additives useful for the formulation of dermally applicable preparations;

with a phase ratio of at most 35% oil to 65% water.

2. The multiple emulsion as claimed in claim 1, wherein the following quantitative ratios of the emulsifier, consistency-imparting agent, or oil and demineralized water correspond to 1-8:2-10:5-32:50-92 (in percent by weight).

3. The multiple emulsion as claimed in claim 1 or 2, wherein the phase inversion temperature of the composition is between 60 and 90°C.

4. The multiple emulsion as claimed in one of the preceding claims, which comprises long-chain, saturated, in particular C_8–C_{18} fatty alcohols and/or glycerol stearates, in particular mono- or distearates, and/or organic hydrogel formers, in particular polyacrylates, xanthan gum or alginates, as stabilizers.

5. The multiple emulsion as claimed in one of the preceding claims, which comprises further oil components, spreaders or emollients, in particular vegetable or animal oils and fats, liquid wax esters, fatty acid esters, paraffin oils and/or silicone oils as additives.

6. The multiple emulsion as claimed in one of the preceding claims, which comprises humectants, in particular glycerol, propylene glycol, butylene glycol and/or sorbitol, as additives.

7. The multiple emulsion as claimed in one of the preceding claims, which comprises preservatives and antioxidants as additives.

8. The multiple emulsion as claimed in one of the preceding claims, which comprises pH-regulating additives for the adjustment of the pH of the emulsion to values in the range from pH 5 to 6.5.

9. The multiple emulsion as claimed in one of the preceding claims, which comprises a multiple particle size of the emulsion of 10–30 µm.

10. A process for the production of an emulsion as claimed in one of claims 1 to 9, which comprises heating the water and oil/emulsifier phase to the PIT of the emulsion and immediately homogenizing without introducing noticeable shear forces into the emulsion and avoiding entry of air up to the solidification limit of the stabilizers with formation of multiple droplet sizes of 10-30 µm and allowing the emulsion formed to cool.

11. The process as claimed in claim 10, which comprises using inclined blade stirrers during the cooling process.

Abstract

A stable multiple emulsion of the W/O/W type is obtained by a phase inversion process in the presence of a nonionic ethoxylated emulsifier of the PEG-phytosterol type with 5 to 26 ethoxylation units, a cloud point of between 50 and 110°C and an HLB of > 10, with the simultaneous use of oils with at least 5% by weight (based on the total emulsion) of components that have a polarity of < 20 mN/m. For stabilization, mixtures of polar waxes (e.g. saturated, long-chain fatty alcohols, glycerol stearates) and/or organic hydrogel formers (e.g. polyacrylates) are employed.